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THE CHEMICAL CONSTITUTION OF A LIGNITIC RESIN

James J. Tietjen and Harold L. Lovell
College of Mineral Industries
Pennsylvania State University
University Park, Pennsylvania

Natural resins are formed in trees as a protective measure when the bark is injured. An exuded viscous liquid covering the injury looses its more volatile components and apparently undergoes polymerization and condensation. These rather stable substances appear to occur in low rank coals in a state similar to their original structure. The lack of chemical investigation of coal resins is undoubtedly associated with the tacit assumption of their similarity to the natural resins and with the observation that their physical appearance suggests less alteration than any other maceral.

Although microscopic resin-forms exist in resin ducts observed in most coals, certain coals contain some macroscopic particles which are probably the coalified product of the original exuded resins. The latter can usually be freed from the associated coal by proper comminuition and separated by gravity methods, although preparation of a "pure" fraction is difficult.

Most studies on coal resins have been limited to their physical description and considerations of recovery techniques. These resins range in color from light yellow to deep brown and in specific gravity from 1.00 to about 1.25. They possess varied solubility characteristics although consistently water insoluble. A wide melting range between 120 and 400°C, contrasts with a nearly constant elemental analysis: 80% carbon, 10% hydrogen and 10% oxygen. A generalized constituent classification representing functional group composition includes: resin acids, resin alcohols, resin esters and resenes. The latter represents hydrocarbons.

The experimental data evaluated in this investigation includes: solubility in alkali and in organic solvents, equivalent weights, melting points, elemental analyses, saponification, correlation with abietic acid and amber properties, 2,4-dinitrophenylhydrazine reaction and absorption spectra.

The coal employed in this study was a North Dakota lignite, of the Paleocene Fort Union formation whose analysis appears in Table 1. The resins studied were recovered from the crushed lignite by a sink-float procedure employing a mixture of n-heptane and carbon tetrachloride (specific gravity, 1.15) as the separation medium. A yield of 0.6 g. of pure resins was

obtained from one kilogram of lignite. The resins varied in color from light yellow to deep red and were arbitrarily separated into the three classes: yellow-light orange, orange, and dark orange-red.

Table 1

Proximate Analysis of Sentinel Butte Lignite

Moisture	20.0%
Ash	8.8%
Volatile Matter	47.5%
Fixed Carbon	23.7%
Moist B.T.U.	7500

Figure 1 shows the reprecipitated acid fraction of the resin color classes to possess essentially identical vibrational characteristics. This is also true for the original resin color classes. The only major dissimilarity appears in the 3 micron region. The darker colored resins apparently have an increased degree of associated hydroxyl vibration. The assignments given to the various absorptions are shown in Table 2. The ultraviolet absorption spectra, Figure 2, show equal similarities between color classes. However, the darker-colored resins undoubtedly have a higher chromophoric concentration. The 215 millimicron absorption maximum and the visible absorption data (Figure 8) suggest a conjugated carbonyl structure. This possibility is confirmed by a positive test for a ketone by formation of a dark orange-red 2,4-dinitrophenylhydrazone.

Table 2

Infrared Absorption Assignments of the Resins and Resin Acids

Wavelength (microns)	Vibrational Assignment
2.93	O-H stretch (unassociated)
3.05	O-H stretch (associated)
3.42	C-H stretch (aliphatic)
5.80 (shoulder)	C=O stretch
5.89	C=O stretch
6.81	C-H bend (aliphatic)
6.88	C-H Bend (aliphatic)
7.25	CH_3 symmetrical bend
8.0-9.0	C-O stretch
9.19	ring vibration
9.72	ring vibration
10.26	C-H bend, or ring vibration
11.30	C-H bend

The noted variation in the dark colored resins is consistent with other observations. The equivalent weights have lower values (Table 3) as do the melting point ranges (Table 4). In addition, the dark-colored resins are more soluble in a number of common organic solvents (Table 5).

The melting range and solubility data indicate the dark-colored resins to be a lower molecular weight material. However, since the spectral data indicate all the resin color classes to have essentially the same structure, it appears that differences in molecular weight must result from varying degrees of condensation of some basic structural unit. Saponification studies are in agreement with this conclusion. The saponified products of both the orange and yellow-light orange resin acids have common equivalent weights. It is suggested that the major portion of these resins, the resin acids, are at least in part composed of a basic unit structure condensed in the form of an ester.

In considering the nature of this basic unit, it seems logical to pursue an investigation of abietic acid which has been studied extensively in dealing with natural plant resins. The oxidation tendencies of abietic acid are especially significant.

As abietic acid undergoes slow air-oxidation (Figure 3) its infrared absorption spectra becomes increasingly similar to that of the resin acids. The major changes are associated with the higher oxygen content (lower carbon and hydrogen values - Table 6) and the decreased crystallinity (amorphorous appearance and lower melting range - Table 4) of the oxidation products. A second carbonyl band appears at 5.80 microns, and the absorption in the 8.0 to 9.0 micron region, corresponding to C-O stretching vibrations, is increased. The decrease in the crystalline nature of oxidized abietic acid is also markedly reflected in the infrared spectra. The destruction of at least part of the unsaturated structure by oxidation is indicated by the decreased band at 7.82 microns, corresponding to the $> C = CH$ group.

Related effects are noted in the ultraviolet absorption spectra (Figure 4). These are in general associated with the conjugated double bonds. The 241 millimicron band maximum decreases and a new absorption appears at 215 millimicrons indicating that the total unsaturated character is not destroyed, but that one of the double bands remains in conjugation with the carbonyl group formed by the oxidation.

Although similar, the infrared absorption spectra of the resin and that of air-oxidized abietic acid are not identical. The resin apparently has a higher aliphatic C-H content and possesses three unique bands at 9.72, 10.26 and 11.30 microns. These latter absorptions are found in amber, a natural resin which is considered to be a mixture of succino-abietic acid and esters of succinic acid. It is characterisitcally insoluble in acetic acid.

The resins yield a glacial acetic acid-soluble fraction which is darker in color, has a lower melting range and lower carbon-hydrogen content than the original. The infrared spectra of the acetic acid-soluble resin fraction and the air-oxidized abietic acid (Figure 5) are very similar,

Table 3

Equivalent Weight Determinations

Sample		Equivalent Weight
A. Precipitated resin acids		
1. Yellow-light orange		726
		748
	Average	737
2. Orange		648
		660
	Average	654
3. Dark orange-red		556
		535
	Average	546
B. Saponified resin acids		
1. Yellow-light orange		325
		341
	Average	333
2. Orange		327
		332
		340
	Average	333
C. Glacial acetic acid insoluble fraction		
1. Yellow-light orange		495
2. Orange		433
		444
	Average	439
D. Abietic acid		
1. Pure		299
		301
		303
	Average	301
2. "Air-oxidized", 15 years		336
		337
		334
	Average	336

Table 4

Melting Point Data

Sample	Melting Range(°C)
A. Resins	
1. Yellow-light orange	185-210
2. Orange	180-205
3. Dark orange-red	170-190
B. Precipitated resin acid (orange)	180-210
C. Acetic acid soluble fraction (orange resins)	141-167
D. Acetic acid insoluble fraction (orange resins)	220-295
E. Abietic acid	
1. Pure	162-164
2. "air-oxidized" for fifteen years	91-95
F. Amber	245-325

Table 5

Resin Solubility Tests in Organic Solvents

Solvent	Yellow-Light Orange	Orange	Dark Orange-Red
Acetone	Slightly soluble	Very soluble	Completely soluble
Chloroform	Insoluble	Slightly soluble	Slightly soluble
Ethanol	Slightly soluble	Very soluble	Completely soluble
Glacial Acetic Acid	Very soluble	Very soluble	Very soluble
Benzene	Insoluble	Slightly soluble	Slightly soluble

Table 6

Results of Elemental Analyses and Mol. Wt. Determinations

Sample	%C	%H	%N	%S	%Ash	Mol. Wt.
Resin (orange)	78.8	10.0	0.8	none	none	---
Precipitated resin acids (orange)	78.5	10.1	0.3	---	---	635
Glacial acetic acid soluble fractions						
1. Yellow-light orange	75.8	9.4	---	---	---	---
2. Orange	75.0	9.4	---	---	---	---
	75.1	9.6	---	---	---	---
Abietic Acid						
1. Pure	79.6	10.2	---	---	---	---
	79.5	10.1	---	---	---	---
a. Theoretical	79.4	10.0	---	---	---	---
2. "Air-oxidized" for two years	77.1	9.6	---	---	---	---
	77.1	9.5	---	---	---	---
3. "Air-oxidized" for for fifteen years	70.3	8.4	---	---	---	---

especially in respect to the decreased absorptions at 9.72, 10.26 and 11.30 microns which are related to amber. The infrared spectra of the glacial acetic acid-solubles and insolubles are strikingly different. The latter closely approximates the spectrum of natural amber. The strong hydroxyl band at 2.93 microns, in the amber spectrum, is a dissimilarity, but is in agreement with the less intense carbonyl bands observed. Supporting evidence is indicated in the ultraviolet absorption spectra of the soluble compound, Figure 6, and of the insoluble fraction, Figure 7. The data suggest complete isolation of these compounds was not attained.

By assigning the 11.30 micron absorption to amber, the spectra of the original resin color-classes may be interpreted to indicate a constant level of amber concentration. Therefore, the variation in equivalent weights of the differently colored resin acids, cannot be related to varying amber concentrations. The difference in the equivalent weights of the amber-like fraction (acetic acid-insoluble) obtained from the yellow-light orange, and orange resins is not diverse enough to account for the difference in the equivalent weights of the corresponding resin's acids. Since it has been indicated that slight mutual contamination exists in the two acetic acid-solubility fractions, one may conclude that the equivalent weight of the amber is constant, but that of the oxidized-abietic acid fraction varies. This property of the oxidized-abietic acid-like fractions (acetic acid-soluble) decreases with increasing resin color intensity.

Since it has been shown earlier that saponification reduces the equivalent weights of the differently colored resin acids to a common value, it seems that the "oxidized abietic acid-like" material exists as an ester. This is possible, since the oxidation products of abietic acid have been shown to have hydroxyl groupings, and could enter into self-condensation reactions. A possibility of an abietate other than a self-condensation product is discounted because of the simplicity of the spectra, and because of a high molecular weight alcohol would have been insoluble in the alkaline solution after saponification. Such a self-condensation reaction could also account for the differences in color of the resins and their corresponding acids, if the condensation involved a secondary hydroxyl group that might otherwise be oxidized to a chromophoric carbonyl group.

It is concluded that the resins separated from this North Dakota lignite have undergone only a moderate degree of alteration during the coalification process, that they are composed of a mixture of amber (succino-abietic acid and esters of succinic acid) and a form of oxidized-abietic acid. It is suggested that the oxidized-abietic acid component has undergone self-condensation to form an ester.

ACKNOWLEDGEMENT

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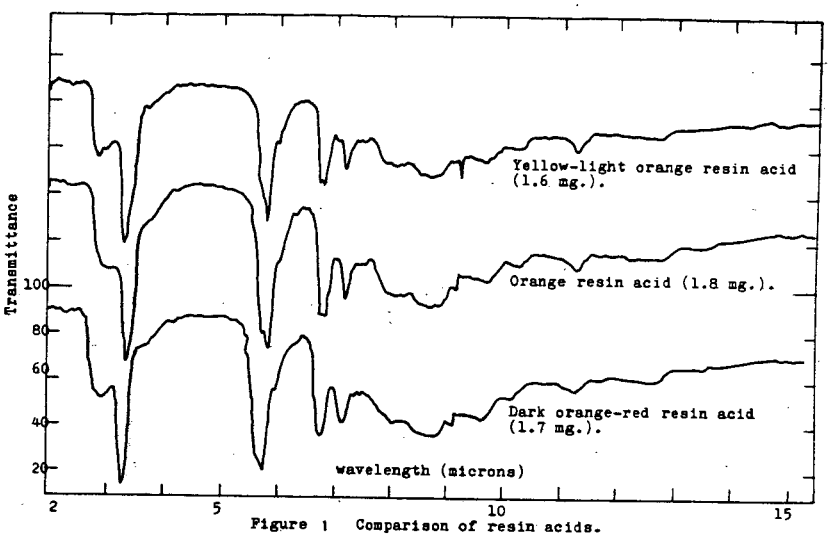

Figure 1 Comparison of resin acids.

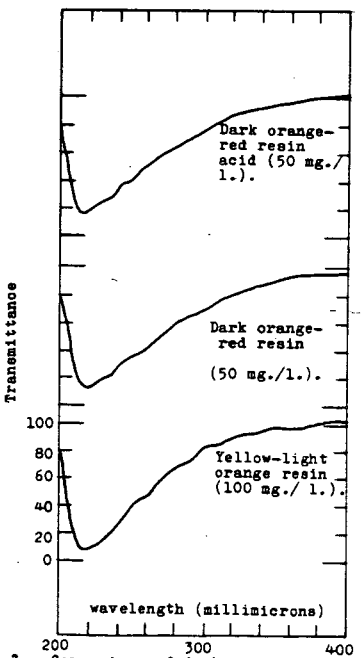

Figure 2 Comparison of dark-orange red resin and resin acid with yellow-light orange resin.

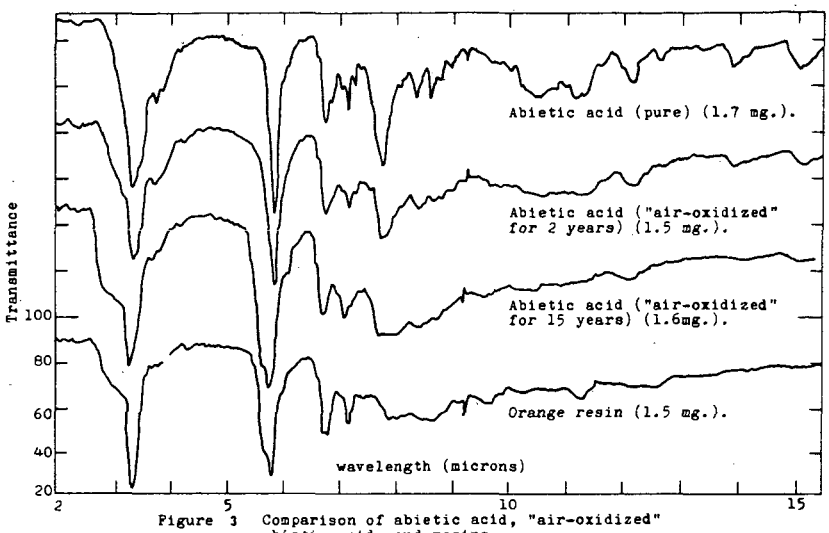

Figure 3 Comparison of abietic acid, "air-oxidized" abietic acid, and resins.

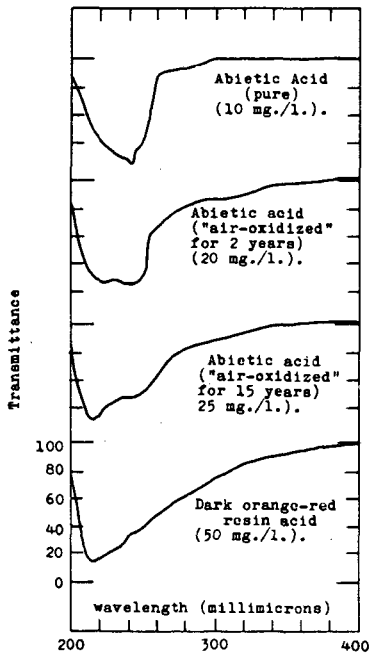

Figure 4 Comparison of abietic acid, "air-oxidized" abietic acid, and resin.

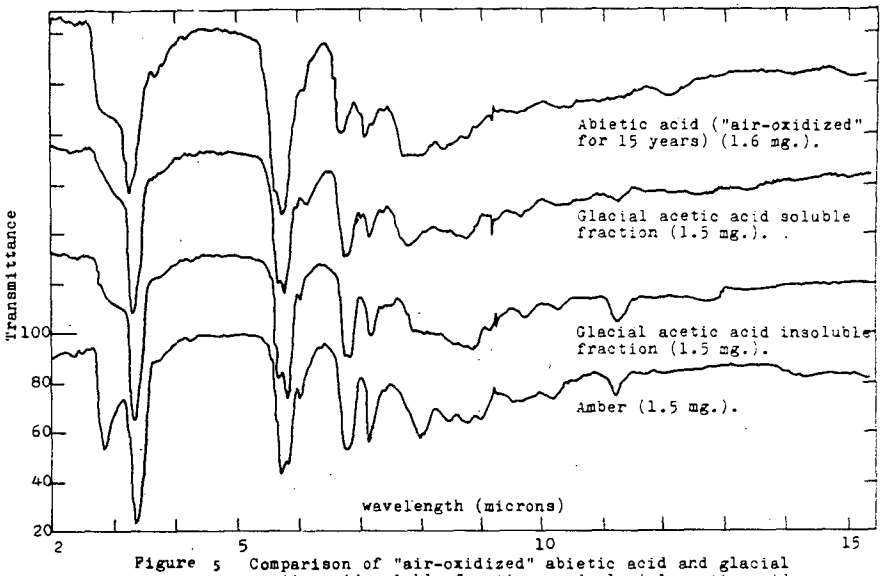

Figure 5 Comparison of "air-oxidized" abietic acid and glacial acetic acid soluble fraction, and glacial acetic acid insoluble fraction and amber.

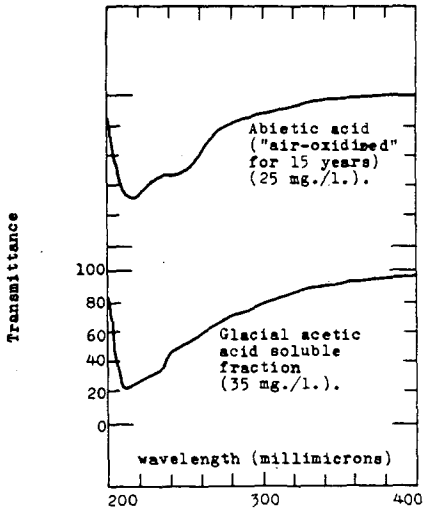

Figure 6 Comparison of glacial acetic acid soluble fraction and "air-oxidized" abietic acid.

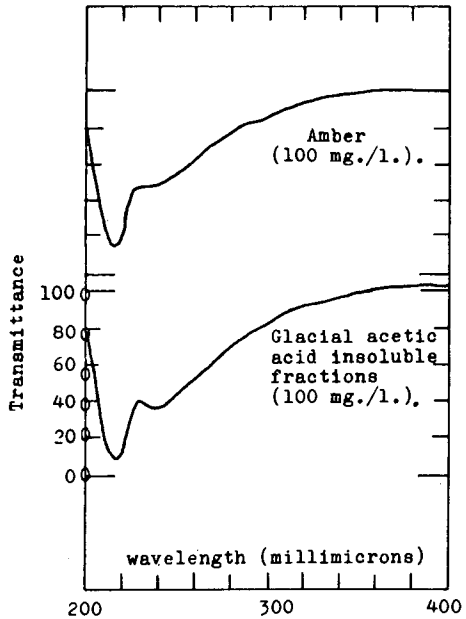

Figure 7 Comparison of amber and glacial acetic acid insoluble fraction.

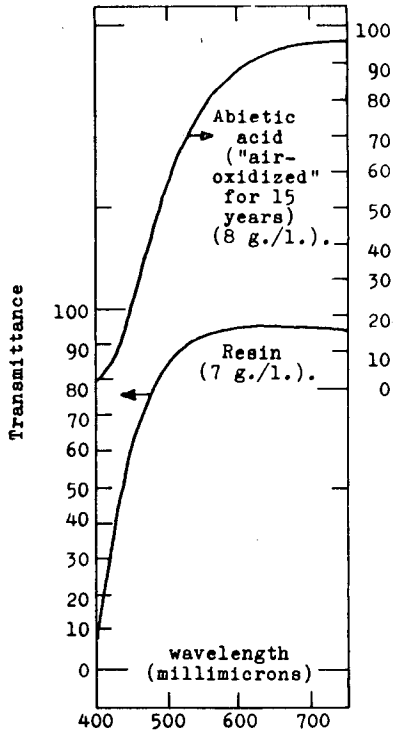

Figure 8 Comparison of resin and "air-oxidized" abietic acid.